

## Appendix 8. Estimating rates of water drainage through the unsaturated zone at the East Poplar oil field on the basis of concentration profiles of chloride and nitrate, 2006

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The rate of water drainage through the unsaturated zone can be estimated on the basis of concentrations of certain chemicals within pore waters, provided certain conditions are met. Two methods are appropriate for this study: the chloride (or nitrate) deposition method and the peak displacement method (Scanlon and others, 2002; Scanlon, 2010).

The chloride deposition method is predicated on the assumptions that all chloride residing in the unsaturated zone is derived from atmospheric deposition and that there is no change in the amount of chloride stored within the interval of the unsaturated zone being studied. A simple chloride mass balance is then assumed:

$$Dep_{Cl} = qC_{uz} \quad (1)$$

where  $Dep_{Cl}$  is the annual rate of chloride deposition,  $q$  is average annual drainage rate within the unsaturated zone, and  $C_{uz}$  is chloride concentration in the unsaturated zone. Chloride deposition occurs in wet (dissolved in precipitation) and dry (dust) phases. Wet deposition can be represented as the product of annual precipitation rate,  $P$ , and average chloride concentration in precipitation,  $C_p$ . Long-term annual precipitation data are available from nearby National Weather Service stations. Chloride concentration in precipitation is measured at a National Atmospheric Deposition (NADP) site that is located near the study area. Historical data on dry deposition rates are not available, so for purposes of this study it is assumed that dry deposition rates were equal to wet deposition rates. Hence, equation (1) can be rewritten as:

$$q = 2PC_p/C_{uz} \quad (2)$$

$C_{uz}$  is determined by collecting soil water samples across a depth profile through the unsaturated zone. This method can be applied with nitrate as well as chloride data.

The peak-displacement method does not require an estimate of atmospheric deposition rates but does require a unique tracer. The method tracks the movement of a chemical or isotopic tracer over time. The tracer can be applied intentionally or unintentionally; in addition, natural tracers can sometimes be used in this method to identify changes in climate or land use (Scanlon, 2010). For the current study, oil-field brines that were released to the land surface at some point in the past can serve as tracers. By collecting soil cores and analyzing the soil cores for chloride concentration, the depth of the peak chloride concentration can be determined. If cores are collected at two different times ( $t_0$  and  $t_1$ ), then the velocity of peak displacement is calculated as:

$$v = (z_1 - z_0)/(t_1 - t_0) \quad (3)$$

Where  $v$  is average vertical velocity of the concentration peak, and  $z_1$  is depth of tracer peak concentration at time  $t_1$ . Vertical drainage can then be calculated as:

$$q = v\theta \quad (4)$$

where  $\theta$  is volumetric water content (water content by weight multiplied by soil bulk density).

### **Data collection**

Soil cores were collected at 11 locations (fig. 5) during August 2006 by using a Geoprobe pneumatic drill rig. Continuous 2-inch cores were collected in 4-foot (ft) sample barrels to a depth of about 30 ft at each site. Cores were removed immediately from the 4-ft sample barrels, and samples at approximately 1-ft intervals were collected and placed in soil tins. Lids were secured to the tins with electrical tape. The tins were transported to the U.S. Geological Survey Unsaturated Zone Field Studies laboratory in Lakewood, Colorado, where water content by weight was determined according to the method described in Dane and Topp (2002). Water-leachable concentrations of chloride and nitrate in sediment samples were determined according to the method described by McMahon and others (2003); sediment was dried at 50 °C for several days, 10 grams of dried sediment were placed in a dry beaker, and 90 grams of deionized water was added. After mixing, samples were placed on an orbital shaker for 1 hour at 170 revolutions per minute. The samples were then spun on a centrifuge for 10 minutes, after which water was extracted from the samples through a 0.45-micron filter. Chloride and nitrate concentrations in the water extracts were determined with an ion chromatograph (Dionex Corporation, 2001).

### **Results**

Water content and chloride and nitrate concentrations for samples at the 11 sampling sites are given in appendix 9. Cores R1-A and R1-B were located on a rather steep ridge with shallow depths to bedrock; this area has never been cultivated, nor has there been any oil-development activity in the proximity. These locations are presumed to represent a natural environment, unaffected by human activity. Chloride and nitrate concentrations at R1-A are relatively consistent with depth, within an approximate range of 1 to 20 mg/L (appendix 9). Similar concentrations were found at location R1-B, except for a large bulge in chloride concentration at depths of 5 to 9 ft. Concentration bulges such as this are naturally occurring phenomena in arid and semiarid regions of the United States (Healy and others, 2008); these bulges are thought to represent zones of chloride accumulation where plants have extracted soil water but left the chloride in the soil (Phillips, 1994). Human activity can displace these bulges. Depth-concentration profiles for sites M30, O6-9, and R13-A also seem to reflect natural conditions unaffected by human activity.

Other sites appear to be affected by agricultural activity (in respect to chloride concentrations); 06-3, 06-5, R12-A, and possibly 93-4 have chloride concentrations that consistently are about 10 times greater than boreholes that are unaffected by human activity. The consistency in concentrations in these boreholes suggests regular application of chloride, perhaps as a component of agricultural chemicals such as potash (potassium-

chloride). In the absence of records of agricultural chemical application rates, the chloride deposition method cannot be applied for these four sites; however, nitrate concentration profiles in these boreholes are similar to those in the unaffected boreholes (appendix 9), so application of the nitrate deposition method is appropriate.

Average annual atmospheric deposition rates for chloride (0.15 kilogram per hectare per year) and nitrate (0.56 kilogram per hectare per year as N) were obtained through the National Atmospheric Deposition Program (<http://nadp.sws.uiuc.edu>; accessed March 9, 2010). Average flux rates through the unsaturated zone were calculated by the chloride or nitrate deposition methods (equation 2) using these parameter values and average concentrations in the soil profiles that did not appear to be contaminated by agricultural or oil-field activity (appendix 10).

The chloride concentration-depth profiles for boreholes 92-6 and 93-3 suggest an alternative source of chloride, such as release of brine from oil-field operation. Peak concentrations of about 3,000 milligrams per liter (mg/L) at the 12-13-ft depth (92-6) and 10,000 mg/L at the 16.5-ft depth (93-3) are much greater than concentrations expected from natural or agricultural chloride sources. If the source of these high concentrations was a release of brine on the land surface, and if the date of that release can be estimated, then the peak-displacement method can be used to estimate the rate of vertical movement of the concentration peak.

The date of a brine spill at site 93-3 is unknown; however, soil samples were collected near this location in 1989 and analyzed for chloride (Scott Brown, Montana Salinity Control Association, written commun., 1989). Chloride concentration in soil was measured at 2,400 milligrams per kilogram (mg/kg) of soil over the depth interval of 24 to 48 inches. If it is assumed that the peak concentration in 1989 was at 4 ft, then equations 3 and 4 provide an average annual drainage rate of 5.8 centimeters per year (cm/y), with volumetric water content ( $\theta$ ) estimated to be 0.265 on the basis of measured water contents (appendix 9) and an assumed bulk density of 1.65 grams per cubic centimeter. If the actual depth of peak concentration in 1989 is deeper than 4 ft, the calculated drainage rate would be less.

Historical aerial photographs indicate that brine releases caused land scarring in the vicinity of borehole 92-6 between 1956 and 1967 (photograph sources listed in table 1). If equations 3 and 4 are applied with  $\theta$  estimated to be 0.12 and assumed brine release date between 1956 and 1967, the estimated drainage rate would be between 0.9 and 1.2 cm/y.

In summary, chloride and nitrate concentrations in unsaturated-zone pore water were measured at 11 sites in the East Poplar oil field study area. Rates of water drainage through the unsaturated zone were estimated with the chloride and nitrate deposition methods and the peak-displacement method. Estimated drainage rates ranged from 0.07 to 5.9 cm/y.